Far-Infrared Spectroscopy Group(Annual Report)

journal or publication title	The science reports of the Tohoku University. Ser. 8, Physics and astronomy
volume	9
number	1
page range	67-70
year	1988-07-25
URL	http://hdl.handle.net/10097/25665

Far-Infrared Spectroscopy Group

Academic Staff

Associate Professor	Mikihiko Ikezawa
Research Physicist	Takao Nanba
Technical Staff	Toshio Chiba
Graduate Students	Itsuro Yamamoto (D3), Xiao-lei Wang (D1)
	Takashi Satoi (M1)
Guest	Teruyoshi Awano (Tohoku Gakuin University)

Research Activities

(I)Far-Infrared Spectroscopy by Synchrotron Radiation

a. Black Phosphorus Crystal (T. Nanba and M. Ikezawa)

The observation of the reflectivity spectra have been continued using a small specimen with the diameter of 3 mm using a long wavelength spectroscopic system, which has been constructed at the beam line BL6A1 in the UVSOR Facility of the Institute for Molecular Science under the direction of Prof. H. Inokuchi in collaboration with the UVSOR staffs. The TO and LO frequencies of the B_{1u} mode which is polarized along the x-direction of the crystal have been determined as 127.5 and 133.9 cm^{-1}. This is the first precise observation of the Lydane-Sachs-Teller splitting in the homopolar materials.

b. Millimeter Wave Absorption in Ge Crystal (T. Nanba and M. Ikezawa)

The absorption spectrum of a pure Ge crystal was measured in the wavenumber region from 3 to 30 cm^{-1} at BL6A1. A distinct absorption peak was found at 8 cm^{-1} at 300 K which vanished at 80 K. From the temperature dependence of its intensity, the lowlying absorption is considered to be due to a two-phonon difference process.

c. Super Ionic Conductors Rb_4AgI_5 and KAg_4I_5 (T. Awano, T. Nanba and M. Ikezawa)

Reflectivity spectra of these crystals were measured in the spectral region from 5 to 200 cm^{-1} at a temperature between 15 and 300 K. More than fifty absorption bands were resolved at 15 K. Optical conductivity and dielectric constants were calculated by the Kramers-Kronig analysis. Lattice vibrational bands near 100 cm^{-1} shifted by a few tens wavenumbers to high energy side in KAg_4I_5 compared with $RbAg_4I_5$. In both crystals bands were found at 6 and 8 cm^{-1}. At 300 K a broad absorption band seems to locate its peak at 0 cm^{-1} and its intensity decreased at low temperature.

d. Spectroscopy Under High Pressure (T. Nanba)

Transmission measurement system at low temperature and under high pressure up to 10 GPa in a diamond anvil cell has been designed and is now under construction at BL6A1.

(II) Optical Properties of Materials

a. Optical Properties of High Tc Superconductors of $YBa_2Cu_3O_{7-\delta}$ Crystals (X. Wang, T.Nanba and M. Ikezawa)

Reflectivity spectra from the infrared to VUV region (0.05 to 30 eV) have been measured at room temperature with single crystals which were grown by Prof. S. Hayashi and Prof. H. Komatsu of the Institute of Materials Research. The VUV measurement was done at the storage ring of ISSP, Tokyo University. In the infrared region below 1.5 eV, the spectra of the both crystals are interpreted well by the Drude theory of the free carriers with the extremely short relaxation time of 10^{-16} to 10^{-15} s. In the visible to the VUV region absorption structure due to the band-to-band transition were observed. In $YBa_2Cu_3O_{7-\delta}$ the structure of the overall shape of the absorption spectrum are similar to a calculated one by Zhao *et al*. based on the energy band theory but the energies at the observed structure are 1 to 2 eV higher than the calculation.

b. LaB_6, CeB_6 and SmB_6. (T. Nanba, S. Kimura and M. Ikezawa)

Absorption measurement has been continued in the wide wavelength resion from far-infrared to VUV, or from 0.002 to 25 eV. The Drude edge was observed at 2.05 eV in LaB_6 and at 2.0 eV in CeB_6 and SmB_6. Below the edge anomalous dip structure in the reflectivity spectra were confirmed in the *f*-electron system of CeB_6 and SmB_6. Also in the far-infrared region these crystals showed dips in the reflectivity spectra at about 100 cm^{-1} when they were cooled down to 10 K in contrast to LaB_6 which showed the usual metallic reflectivity. In the UV region absorption structure has been observed which can be attributed to *p-d* transition between the valence and conduction bands. Detailed study in the whole energy region is in progress.

c. A Hole Trapped Center in Alkali Silver Halides (T. Awano and M. Ikezawa)

In collaboration with Dr. T. Matsuyama and Prof. H. Yamaoka of Institute of Research Reactor, Kyoto University, radiation damage effects in the alkali silver halides of K_2AgI_3 and Rb_2AgI_3 have been studied by optical and ESR observations. γ-ray irradiation at 77 K induces the same defects as those induced by X-ray in these crystals. The analyses of the hyperfine and the super-hyperfine structure in the ESR spectra show that a hole is trapped mainly at an iodine ion and it is weakly coupled to an alkali ion of K^+ or Rb^+. The color center has a symmetry axis along the direction from the iodine to the alkali ion. ESR parameters are $g_{//}=2.00$, $g_{\perp}=2.15$, $A_{//}=530$ G and $A_{\perp}=215$ G. Iodine ions at two sites, out of three different sites in the unit cell, form the hole center. The optical absorption spectra of the center measured with the linearly polarized light along the *a*-, *b*- and *c*-axis of the crystal have main peaks at about 2.9, 2.5 and 3.2 eV, respectively, in Rb_2AgI_3. The respective peaks in K_2AgI_3 are at about 2.9, 2.5 and 3.1 eV.

d. Color Centers in Super Ionic Conductors $RbAg_4I_5$ and KAg_4I_5 (T. Awano and M. Ikezawa)

Similar absorption bands were found to be induced in these crystals by γ-ray irradiation at 77 K, which indicates that defects of the same structure were

formed in the two crystals. Optical bleaching was observed to examine the correlation between the formed bands. The induced bands at 1.80 and 2.35 eV in $RbAg_4I_5$ and bands at 1.75 and 2.4 eV in KAg_4I_5 were bleached by light illumination at 1.80 eV or at 1.75 eV in each crystal. The two bands were also bleached by illumination in the 2.85 eV band in $RbAg_4I_5$ or in the 2.9 eV band in KAg_4I_5 but in this case the 2.89 or 2.9 eV band itself was not bleached. Observations are in progress.

(III) Surface Enhanced Raman Scattering (SERS)

a. CO on Ag (I. Yamamoto and T. Nanba)

We have continued the observation of the frequency shift of the stretching mode of CO chemisorbed on Ag film which was induced by coadsobate of chlorine. It induced an upward shift beyond the peak position of free CO stretching mode at 2142 cm^{-1}, as was expected from our model which explains the change in the adsorption state of CO due to the coadsorption in relation to an electronegativity of the coadsorbate.

b. CO on Cu and Au (T. Nanba, T. Satoi and S. Kimura)

C-O stretching Raman bands of chemisorbed CO on copper and gold films were found at 2100 and 2120 cm^{-1} at 80 K. In these metals the electron-hole recombination luminescence by the excitation of the *d*-electron to the conduction band was strongly excited by the 5145 or 4880 A light of the argon ion laser. Therefore, the excitation by the red lines at 6471 and 6764 A of a krypton laser was required to resolve rather weak SERS signal superposed on the intense back ground spectrum of the luminescence.

c. The Change in the Surface Potential of Silver Films (T. Nanba and T. Satoi)

The changes in the surface potential of the silver film due to the adsorption of different materials were measured in a ultra high vacuum chamber by the retarding potential method. We found that the coadsorbation of Kr atoms with pre-adsorbed CO on silver induced the decrease in the surface potential which forms a part of the work function of the substrate. In contrast, the coadsorption of oxygen molecules with CO at 80 K induced the increase of the surface potential. These results confirm the proposed model which correlates the electronegativity of the coadsorbed materials with the change in the adsorption state of CO on silver film induced by the coadsorption of rare gas atoms and oxygen.

Publications

1) Far-Infrared Spectroscopy of Small Solid State Specimens,
T.Nanba, Y. Urashima, M. Ikezawa, M. Watanabe and H. Inokuchi,
UVSOR Activity Report 1986(April 1987) p.64.
2) Radiation Damage in Super Ionic Conductors of $RbAg_4I_5$ and KAg_4I_5,
M. Ikezawa, T. Nanba, T. Awano, T. Matsuyama and H. Yamaoka,
Technical Report of the Research Reactor Institute, Kyoto University (June 1987)
KURRI-TR-292, p.65 (in Japanese).
3) Optical Properties of Polycrystalline $YBa_2Cu_3O_{7-\delta}$,
X. Wang, T. Nanba, M. Ikezawa, Y. Ishikawa, K. Mori, K. Kobayashi, K. Kasai,
K. Sato and T. Fukase,
Jpn. J. Appl. Phys. 26(1987)L1391.
4) Optical Reflectivity of Single Crystals of $YBa_2Cu_3O_{7-\delta}$ and $ErBa_2Cu_3O_{7-\delta}$,
X. Wang, T. Nanba, M. Ikezawa, S. Hayashi and H. Komatsu,
Jpn. J. Appl. Phys. 26(1987)L2023.
5) Synchrotron Radiation as a Light Source in the Submillimeter and Millimeter
Wave Regions, Twelfth International Conference on Infrared and Millimeter Waves
(December 1987), Conference Digest, p.45.
6) Anisotropic Reflectivity of Black Phosphorus in the Far-Infrared Region,
T. Nanba, M. Ikezawa, I. Shirotani and H. Inokuchi, *ibid*.p.231.
7) Radiation Damage Effect in Alkali Silver Halide Crystals,
M. Ikezawa, T. Nanba, T. Awano and T. Matsuyama,
Technical Report of the Research Reactor Institute, Kyoto University (January1988),
KURRI-TR-297, p.8 (in Japanese).
8) Far-Infrared Photoacoustic Spectroscopy; Detection System,
T. Masujima, T. Nanba and K. Fukui,
UVSOR Activity Report 1987 (February 1987) p.78.
9) Kondo States of Ce-Compounds: CeB_5, CeTe and $CeIn_3$,
Y. S. Kwon, N. Sato, H. Abe, T. Nanba, S. Kunii, M. Ikezawa, T. Suzuki and
T. Kasuya, *ibid*. p.82.
10)Far-Infrared Absorption Spectrum of Super Ionic Conductor $RbAg_4I_5$,
T. Awano, T. Nanba, M. Ikezawa and M. Watanabe, *ibid*. p.84.
11)A Hole Trapped Center in Alkali Silver Halides,
M. Ikezawa,
Radiation Chemistry No.45 (March 1988) p.45 (in Japanese).